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Luis [DK/DK]; Strandparken 35, DK-4000 Roskilde (DK). **OLSEN, Erling** [DK/DK]; Peterssaeed 4, Svogerslev, DK-4000 Roskilde (DK).

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(74) Agent: **GILL JENNINGS & EVERY**; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).

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(71) Applicant (for all designated States except US): **ROCKWOOL INTERNATIONAL A/S** [DK/DK]; Hovedgaden 584, DK-2640 Hedehusene (DK).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LAURIDSEN, Dan** [DK/DK]; Moellevaenget 5, DK-2800 Lyngby (DK). **PAASKE VOIGT ANDERSEN, Claus** [DK/DK]; Syvhoejvaenge 204, DK-2625 Vallengsbak (DK). **NOVRUP BENGTSON, Jakob** [DK/DK]; Bueparken 62, DK-2750 Ballerup (DK). **OVERTON HOLM, David** [DK/DK]; Hoejagerparken 10 1TV, DK-2750 Ballerup (DK). **PRIMDAHL, Soeren** [DK/DK]; Straedet 7, DK-3550 Slangerup (DK). **JOERGEN NOERGAARD,**

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(54) Title: MINERAL FIBRE PRODUCTS

(57) Abstract: The invention provides a method of making a mineral fibre batt comprising shell-core fibres and other fibres, the method comprising fiberising a melt to form a cloud of said other fibres, collecting said other fibres as a web by air-laying and forming the web into a batt, wherein the shell-core fibres are formed of a silicate network and comprise silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal atoms and have an analysis expressed as percent by weight oxides including at least 3% FeO and 0 to 8% alkali metal oxide and at least 5% MgO, and in the shell-core fibres at least 70% of the iron is ferric and the fibres have a core surrounded by an outer surface layer less than 1 micron thick in which the peak concentration of magnesium atoms is at least 1.5 times the concentration of magnesium atoms in the total fibre, characterised in that the method comprises including the shell-core fibres in the batt by mixing the shell-core fibres with the other fibres after formation of the other fibres but before completion of formation of the batt from the web.

WO 2006/063846 A1

Mineral Fibre Products

We have described in WO 2004/110945 a mineral fibre product comprising fibres formed of a silicate network and comprising silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal atoms characterised in that the fibres have an analysis (expressed as % by weight oxides) including at least 3% FeO and 0 to 8% alkali metal oxide and at least 5% MgO, at least 70% of the iron is ferric and the fibres have a core surrounded by an outer surface layer less than 1 μ m thick in which the peak concentration of magnesium atoms is at least 1.5 times the concentration of magnesium atoms in the total fibre.

We also describe in that application a method of treating mineral fibres formed of a silicate network to improve their high temperature properties wherein the fibres comprise silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal atoms, characterised in that the fibres have an analysis (expressed by weight oxides) including iron in an amount of at least 3% measured as FeO and in which there is at least 2% iron (measured as FeO) present as ferrous iron, 0 to 8% alkali metal oxide and at least 5% MgO, and the method comprises exposing the fibres containing at least 2% by weight ferrous iron under oxidising conditions to a controlled increased temperature which is above the temperature at which oxidation of the iron in the fibres occurs but which is below the temperature at which substantial network crystallisation occurs and thereby oxidising the ferrous iron to provide fibres in which at least 70% of the total iron is ferric.

In a typical example, a mineral charge is melted in a cupola furnace to form a mineral melt which is then fiberised by a centrifugal cascade spinner to form fibres which are collected as a primary web. This is then cross lapped in conventional manner and consolidated to make a batt containing 0.5% oil and organic binder. The binder

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serves primarily as a lubricant and dust suppressant in this process.

The analysis of the fibres (by weight of oxides) is SiO₂ 43.5%, Al₂O₃ 19.0%, TiO₂ 1.1%, FeO 6.0%, CaO 20.3%, MgO 6.6%, Na₂O 2.4%, K₂O 0.3%, P₂O₅ 0.2% and MnO 0.5%.

The batt contains 31.6% shot particles having a diameter above 63µm and it has a median fibre diameter of 4.2µm, with 16% below 2µm and 84% below 7.2µm. The batt is needed in conventional manner. The binder and oil are burnt off in an oven.

The resultant conventional batt is labelled batt X.

In one test, batt X is then passed through a gas blown oven in which the temperature to which the fibres in the batt are subjected is controlled at a value of between 600 and 800°C for between 2 and 90 minutes. For this particular fibre, T_g (glass transition temperature) is 680°C and T_c (crystallisation temperature) is 870°C, both determined by DSC.

The atmosphere in the oven is air and the temperature to which the batt is subjected in the oven is raised from 620°C to about 800°C at a rate of 10°C per minute.

SNMS (Secondary Neutral Mass Spectroscopy) analysis shows that the final product has an analysis for all elements which is substantially uniform up to the outer 0.5µm layer. Between 0.5 and 0.1µm there is a gradual increase in the concentrations of magnesium and calcium and a decrease in the concentration of most other elements, and in the outermost 0.1µm the concentration of calcium and magnesium is significantly increased with a corresponding reduction in the concentration of the other elements.

Monitoring the colour and the weight of the batt as the temperature increases shows that the colour remains unchanged and the weight decreases as the temperature rises to around 550°C (indicating combustion or volatilisation of organics). From around 600°C there is a gradual increase in weight until, at around 870°C, the increase in weight is

around 0.6%. Complete oxidation of 6% ferrous to 6% ferric ion would correspond to a weight increase of 0.67%.

When the treated batt is exposed to a temperature of 1050°C under conditions simulating those in a fire door (i.e., a closed environment) it is brittle but does not significantly shrink and so has maintained its effective fire protection properties. However, when the untreated batt is subjected to the same conditions, it shrinks significantly.

10 In another set of tests starting with untreated product which is the same as batt X, two samples are taken.

One is reference sample X that is not treated further. The other sample Y is pre-oxidised in an electric heated oven at 700°C for 30 minutes.

15 Both the reference sample X and the pre-oxidised sample Y are exposed to a temperature of 1100°C under conditions simulating those in a fire door (ie., a closed environment) according to ISO 834/DIN 4102 Teil 8.

After 90 minutes of testing, the pre-oxidised sample Y is brittle but does not significantly shrink and complies with EN 13501/2. The (average) temperature on the unexposed surface of the pre-oxidised sample Y after 90 minutes of testing is 311°C. However when the reference sample X is subjected to the same conditions it shrinks and sinters significantly. The temperature on the unexposed surface of the untreated sample is 398°C after 90 minutes of testing.

In other examples we show the effect of heating for 90 minutes in an oxidising atmosphere at 600°C, 680°C or 760°C fibres having an analysis by weight of oxides, namely SiO₂ 45.8%, Al₂O₃ 14.9%, TiO₂ 1.6%, FeO 7.6%, CaO 14.3%, MgO 10.9%, Na₂O 2.0%, K₂O 1.0% and P₂O₅ 0.4%.

The SNMS depth profiles of each of the samples were determined for the outer 0.7µm of each sample in respect of Mg, Ca, Fe, Na, Al, Si and K by conventional techniques. The results show that the amount of Mg in the outermost 0.1µm is significantly increased (relative to the normal

concentration, ie. the overall analysis of the fibre) in each of the tests relative to the starting fibre ST1. They also show that the amount of calcium in the outermost 0.1µm is considerably increased for the 600°C and 680°C tests, but there is a lesser increase in this experiment for ST4, at the higher temperature of 760°C.

The fibres may be made by conventional spinning methods, such as a cascade spinner method or a spinning cup method.

For further details, reference should be made to international publication WO 2004/110945.

We refer below to the fibres defined in that application and/or as made by the methods described in that application as "the defined shell-core fibres". The present invention relates to novel applications and uses of the defined shell-core fibres. The invention also relates to novel methods of production of products containing the defined shell-core fibres.

In a first aspect of the invention, we provide a method of making a mineral fibre batt comprising shell-core fibres and other fibres by fiberising a melt to form a cloud of said other fibres and collecting said other fibres as a web by air-laying and forming the air-laid web into a batt, wherein the shell-core fibres are formed of a silicate network and comprise silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal atoms and have an analysis expressed as percent by weight oxides including at least 3% FeO and 0 to 8% alkali metal oxide and at least 5% MgO and at least 70% of the iron in the shell-core fibres is ferric and the fibres have a core surrounded by an outer surface layer less than 1 micron thick in which the peak concentration of magnesium atoms is at least 1.5 times the concentration of magnesium atoms in the total fibre, and in the method shell-core fibres are included in the batt by mixing the shell-core fibres with the other fibres after formation of the other fibres but

before completion of formation of the air laid web into a batt.

By means of this method it is possible to obtain the beneficial properties of the shell-core fibres described in WO 2004/110945 without the necessity to subject the formed batt to heat treatment. It is possible to provide shell-core fibres by treatment of fibres alone or of tufts of fibres, which can be more technically convenient than treatment of an entire batt, and these fibres or tufts can be incorporated into the final batt.

This method can lead to the production of novel products, such as that defined in the second aspect of the invention, which is a heat insulation or fire protection product comprising the shell-core fibres heterogeneously distributed with other mineral fibres within a batt having a density of 10 to 300 kg/m³, optionally sandwiched between foils and/or structural sheets.

The product of the method may also be a product of the type generally described in WO 2004/110945 as having shell-core fibres homogeneously distributed within a batt of other fibres, especially where those other fibres have essentially the same total overall composition as the shell-core fibres.

The density of the batt made in the method of the invention is usually in the range 30 to 300 kg/m³, more commonly 30 to 180 kg/m³. The batt is usually made by collecting the fibres by air-laying, optionally cross-lapping the collected web and then consolidating the product to the desired density.

The other mineral fibres may be of a similar chemical analysis to the defined shell-core fibres or may be different. When the defined shell-core fibres are of rock, stone or slag, the other mineral fibres are usually also of rock, stone or slag.

Generally the shell-core fibres are formed of a silicate network and comprise silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal, as is

conventional for rock, stone and slag fibres. Accordingly, the amount of iron is usually at least 3% FeO, the amount of alkali is relatively low, usually not more than 8% alkali metal oxides, and the amount of magnesium is
5 relatively high, usually at least 5% MgO.

The other fibres preferably have these properties also and more preferably have the same overall composition as the shell-core fibres, although of course the shell-core fibres have a different distribution of the atoms, in
10 particular magnesium.

In the shell-core fibres at least 70% of the iron is present as ferric iron and the fibres have a core which is surrounded by an outer surface layer less than 1 micron thick in which the peak concentration of magnesium atoms is
15 at least 1.5 times the concentration of magnesium atoms in the total fibres.

Preferably the other fibres contain at least 2% ferrous iron as FeO and have a total iron content of at least 3%.

20 In the shell-core fibres, the enriched outer layer of the fibre may comprise magnesium, and usually also calcium, predominantly in the form of simple or complex oxides. The enrichment may comprise small crystals which may be so small they can be termed nano-crystals. It may be more
25 accurate to refer to them as nucleation sites. The crystals or sites are believed to be of calcium and/or magnesium oxides and/or calcium magnesium silicates (optionally also including other atoms such as iron and aluminium), and in particular comprise small crystals or
30 sites of diopside and/or augite and/or spinel.

Preferably the peak concentration of each of calcium and magnesium in the outer layer is at least 1.5, 2, 3 or 4 times, and may be as much as 5 times or even up to 6 or 7 times or more, the concentration in the total fibre. In
35 particular, although good results are obtained with calcium concentrations which are, for instance, 1.2, 2 to 4 times the concentration in the remainder of the fibre, it seems

desirable for the magnesium enrichment to be particularly high, for instance being 3 to 6 times the magnesium concentration in the total fibre.

By saying that the peak concentration of magnesium atom in the layer is at least 1.5 times the concentration in the total fibre we mean that, when the fibre is subjected to SNMS (Scanning Neutron Mass Spectrometry) depth profile analysis and the concentration of magnesium atoms is plotted from the outermost surface inwards (as shown in Figure 1), the peak concentrations of magnesium atoms which are observed in the outer layer are at least 1.5 times the substantially uniform normal concentration of magnesium atoms that will be observed throughout the remainder of the fibre. This substantially uniform concentration is substantially the chemical analysis of the total fibre. Similarly, all other references to concentrations of other elements in the surface layer relate to the concentrations shown by SNMS.

The surface layer can be regarded as the layer over which the magnesium atom concentration (and usually also the calcium atom concentration) is measurably higher than the concentration in the total fibre and this surface layer is below $1\mu\text{m}$ thick and is usually below $0.5\mu\text{m}$ thick. Often the surface layer is 0.1 or 0.2 to $0.5\mu\text{m}$ thick. The peak concentrations discussed above are usually in the outermost 0.01, and often 0.05, μm of the fibre. Accordingly the core (ie excluding the 0.5 or $1\mu\text{m}$ surface layer) will normally have a substantially uniform concentration of most or all of the elements in the fibre, and the highest concentrations of calcium and magnesium atoms are in the outermost $0.05\mu\text{m}$ or $0.1\mu\text{m}$, with transitional concentrations in the intermediate region between the peak concentration and the core inwards of 0.05 or $0.1\mu\text{m}$.

Iron atoms also may be present in the outer surface layer in an amount greater than the amount in the remainder of the fibre, for instance in an amount of 1.1 or 1.2 up to 2 or more times the amount of iron in the remainder of the

fibre. This occurs especially when the amount of calcium is less than 2 times the calcium concentration in the remainder of the fibre, for instance when there is little or no calcium enrichment of the surface layer.

5 However, the predominant characteristic of the iron in the shell-fibres fibre is that it must be substantially ferric and thus at least 70% of the iron in the fibre must be ferric and usually at least 80, 90 or, preferably, at least 95% of the iron is ferric. It seems that ideally
10 substantially 100% of the iron would be ferric. These percentages are based on the weight of iron.

 The shell-core fibres and the other fibres, independently, preferably have the following features of the chemical analysis of the fibres. The chemical analysis
15 refers to the analysis of the total fibre.

 Expressed by weight of oxides, such fibres preferably contain at least 2%, and generally at least 3%, 4% or 5% or more ferrous iron and may contain as much as 10, 12 or even 15% ferrous iron (all expressed as FeO). The total iron
20 content of the fibres is usually at least 3%, most usually 5 to 10% but can be up to 12 or 15% (all expressed as FeO). In the other fibres and those used to produce the shell-core fibres, initially some of the iron may be ferric, but the iron is mainly (at least 50% and often at least 70%)
25 ferrous when the fibres are made under a reducing environment, such as in a cupola furnace.

 As regards the other elements, expressed by weight of oxides, the amount of silicon is usually 35 to 55%, often 38 to 50% (i.e., weight percent SiO₂ based on total
30 oxides). The amount of calcium is usually at least 8%, often 10 to 20% or more, e.g., up to 30 or 35% (by weight CaO). The amount of magnesium is usually at least 5%, often 8 to 15% or more, for instance up to 20 or 25% (by weight MgO). The fibres may be free of alkali but
35 generally contain alkali (by weight Na₂O + K₂O) in amounts of from zero to 8%, usually 1 to 4% or 5%.

The amount of aluminium (as Al_2O_3) is usually 1 to 25%. If it is required that the fibres should be soluble at around pH 7.5 the amount of aluminium is usually from 1 to 10%, usually 1 to 5% (by weight Al_2O_3) but otherwise the
5 amount of aluminium is usually 10 to 25 or 30%. Amounts of aluminium of at least 13%, and preferably at least 16%, are especially preferred when it is required that the fibres should be soluble at pH 4.5 and typical amounts are 16 to 22%.

10 When the fibres are required to have ceramic properties and to have particularly high heat resistance, the fibres may have a high content of Al_2O_3 , of above 25 or 30%, e.g., up to 35%, 40%, or higher.

In the method the other fibres are formed by
15 fiberising a mineral melt, generally by centrifugal fiberisation. Conventional methods of fibre formation may be used, for instance using a spinning cup or a cascade spinner process.

The melt is fiberised to form a cloud of fibres.

20 The fibres are usually entrained in a stream of air close to the fiberising apparatus, in order to carry them away from that apparatus. Usually the air flows or other conditions to which the fibres are exposed between initial fiberisation and collection as a web are all relatively low
25 temperature conditions, as is conventional.

The fibres are collected as a web, usually in the presence of a bonding agent to facilitate handling of the collected product and/or to suppress dust and/or as a lubricant.

30 Subsequent to collecting the fibres as a air-laid web, the web is formed into the final batt. This may involve cross-lapping of the air-laid web to form a secondary web and/or compression of the air-laid web or secondary web to consolidate it into a batt.

35 As mentioned above, the air-laid fibres are generally collected in the presence of a bonding agent and the batt is generally subjected to high temperature to effect curing

of the binder, in a conventional manner, usually by passing it, before or after any compression, through a curing oven.

In the method of the first aspect of the invention, shell-core fibres are mixed with the other fibres before
5 completion of formation of the final batt. Usually the shell-core fibres are mixed with the other fibres before any compression and before any curing of binder.

The shell-core fibres can be mixed with the other fibres after formation of the air-laid web, for instance by
10 including them on the surface of the air-laid web, in particular during the cross-lapping process.

This can be done by any known method of including solid additives on the surface of an air-laid web. Examples of suitable processes are disclosed in, for
15 instance, WO 99/51536.

However, it is preferred to mix the shell-core fibres with the other fibres before they are collected as an air-laid web, namely by including the shell-core fibres in the cloud of fibres in the spinning chamber where fiberisation
20 of the melt takes place.

This can be done by known methods of mixing solid additives into a cloud of fibres which are to form an air-laid web. Generally the shell-core fibres are injected into the cloud of other fibres. They can be in the form of
25 a slurry but are generally added as dry fibres.

Preferably they are injected close to the point at which the other fibres are formed. However, it is also possible to inject them at a point close to where the other fibres are collected. Injecting close to the point of
30 formation of the other fibres assists in providing a homogeneous distribution of the shell-core fibres in the other fibres.

The shell-core fibres may be added in the form of substantially individual fibres. That is, they are not in
35 the form of tufts of many fibres bonded together and any bundles of fibres have size not more than 1 mm, generally not more than 0.5 mm (size being the maximum dimension).

Inclusion of the shell-core fibres as substantially individual fibres is particularly useful when a homogeneous distribution of shell-core fibres throughout the other fibres is required.

5 Alternatively, the method may be devised so as to produce a heterogeneous distribution of the shell-core fibres within the other fibres. This results in a novel product of the second aspect of the invention and this is discussed further below.

10 In the method of the first aspect of the invention the shell-core fibres are preferably produced from waste mineral fibres which have been subjected to a defined heat treatment stage. That is, the shell-core fibres have been produced by treating mineral fibres formed of a silicate
15 network wherein the waste fibres comprise silicon, calcium, magnesium, iron, aluminium, oxygen and optionally alkali metal atoms and have an analysis expressed by weight oxides including iron in an amount of at least 3% measured as FeO and in which there is at least 2% iron (measured as FeO)
20 present as ferrous iron, 0 to 8% alkali metal oxide and at least 5% MgO, the treatment comprising exposing the fibres containing at least 2% ferrous iron under oxidising conditions to a controlled increased temperature which is above the temperature at which oxidation of the iron in the
25 fibres occurs but which is below the temperature at which substantial network crystallisation occurs and thereby oxidising the ferrous iron to provide fibres in which at least 70% of the total iron is ferric, and which are the shell-core fibres for use in the invention.

30 Preferably, where the waste fibres treated have a glass transition temperature T_g and a crystallisation temperature T_c , the temperature to which the fibres are exposed under oxidation conditions is at least $T_g - 50^\circ\text{C}$ and is preferably at least T_g . Preferably it is below T_c .
35 Preferably it is also not more than $T_g + 100^\circ\text{C}$.

 Preferably the controlled increased temperature is increased during the heat treatment process. Preferably

the rate of increase of the temperature to which the fibres are subjected at temperatures above $T_g - 20^\circ\text{C}$ is less than 20°C per minute.

It is preferred that the waste fibres are recycled fibres, namely fibres taken from the same production environment which is producing the other fibres. For instance they may be fibres taken from the same line into which they are then recycled. Alternatively, they may be taken from a different line in the same production facility.

Generally the recycled fibres are produced within one week, usually within one day, of their recycling into the method of the invention.

This provides a particularly technically convenient method of producing products which contain a blend of shell-core fibres and other fibres and hence have the desirable properties described in WO 2004/110945.

The recycled fibres can for instance be edge trim or batts which are not otherwise to be used.

In the case of edge trim the product can be subjected to heat treatment without any further pre-treatment but preferably the waste fibres are subjected to granulation before heat treatment. We believe this renders the heat treatment process more effective across all of the fibres subjected to heat treatment.

The heat treatment can be carried out by any heating means as described in WO 2004/110945.

Generally the heat treatment under oxidising conditions is conducted for at least 2 minutes, usually more than 10 minutes, e.g. 30 to 100 minutes.

Throughout the range at which oxidation is occurring, it is often desirable that the temperature should be increased in a controlled manner rather than in a random or sudden manner. It may be satisfactory to introduce fibres into an oven at the desired temperature but often it is desirable for the oven temperature to be increased in a controlled manner over a range starting at a temperature

which may be as low as 100°C or 50°C below T_g, and is preferably at least 20°C below T_g and which extends up to a temperature of, for instance, at least 30°C and preferably at least 50°C and often up to 100°C above T_g,
5 although preferably the maximum temperature is always below T_c. If a constant temperature is used it is preferably not too high, for instance it is preferably below T_g + 100°C, and often below T_g + 50°C.

The controlled increase is preferably performed so
10 that the temperature of the fibres increases by a rate of not more than 30°C per minute and preferably less than 20°C per minute, most preferably 2 to 10°C per minute, e.g., 5°C per minute.

The heat treatment is preferably carried out at a
15 temperature of from 600 to 900°C.

The heating means may be coupled to any heating means on the production line, such as the curing oven or, where a cupola furnace is used, the cupola or the after-burner for exhaust gas. Preferably however the heating means is
20 a separate unit.

As an example, in one system for use in the invention, the waste fibre obtained from edge trim is broken down into a granulate which is more convenient to handle than larger pieces of waste fibre material. The granulate is then fed
25 to a heating chamber that is heated by a gas burner. In the heating chamber the granulate is converted to shell-core fibres. The heated and converted granulate is led to a cyclone that separates hot air from the granulate. The hot air from the cyclone is recycled to a pre-heater in
30 order to pre-heat the ambient air fed to the burner. The ambient air is fed into the heat exchanger via a pump.

Subsequent to the formation of the shell-core fibres from the waste fibres the shell-core fibres can be transferred directly to the production process and mixed
35 with the other fibres but preferably are collected in a storage container such as a hopper, from where they can then be fed back into the production process. This is

preferred as providing greater control over the amount of shell-core fibres added into the production process.

When the shell-core fibres are fed into the spinning chamber they may be introduced in such a way that they are
5 homogeneously mixed with the other fibres. Alternatively they can be introduced into the cloud of fibres in such a way that the final product has a layered structure with one or more layers containing predominantly shell-core fibres and one or more layers containing predominantly other
10 fibres. This can be done by controlling where the shell-core fibres are blown into the spinning chamber and the cloud of fibres.

Where the shell-core fibres are formed from waste fibres from the production process producing the mineral
15 fibre batt, the recycling is preferably a continuous process where the waste fibre material is continuously led to heating means to undergo heat treatment.

The proportions typically utilise 10 to 90%, often 20 to 70%, of the defined shell-core fibres with the balance
20 being the other fibres.

An advantage of the process of the invention is that it provides a technically convenient means of controlling to a precise level the proportions of shell-core fibres relative to other fibres.

25 As mentioned above, when the distribution of shell-core fibres within the other fibres is heterogeneous, the product is a novel product.

The heterogeneous distribution may exist as a result of the batt having been formed by collecting tufts of the defined shell core fibres in admixture with free fibres
30 and/or tufts of the other mineral fibres or by collecting free fibres of the defined shell core fibres with tufts of the other fibres.

A preferred method involves blowing tufts of the defined shell core fibres into a cloud of the other fibres
35 as they travel from a spinner by which they are formed towards a collector on which the mixture is collected. The

tufts should be blown into the cloud as close as possible to the spinner in order to achieve a good mixture thereof.

The tufts of the defined shell core fibres may be obtained by comminution of a web or batt of the fibres after the heat treatment which provides the shell core configuration. The tufts of either or both types of fibres may, before being collected, have been bonded, for instance as a result of comminuting a prebonded web into tufts, or the tufts may be unbonded when they are first collected.

By referring to tufts we mean fibre bundles having a sufficiently large size that their presence can be determined by observation of the final product. Typically a substantial proportion of the tufts have a size of at least 3mm, and often at least 5, 10 or 20mm. Thus the heterogeneous product is a distribution of these relatively large tufts of one of the types of fibres with free fibres or tufts of the other fibre.

Irrespective of whether the tufts were bonded before collection into the batt, the collected tufts may contain, or have applied to them, uncured bonding agent and the batt may be subjected to subsequent curing so as to bond the tufts to one another and to any free fibres.

Another product having the heterogeneous distribution is one in which there is at least one layer of the defined shell-core fibres and at least one layer of the other mineral fibres within the batt, i.e., in between any sandwiching high density wool or other structural sheets which sandwich the sides of the batt.

The layers may extend substantially in the plane of the batt, in which event there are preferably at least two layers of the defined shell-core fibres separated by a layer of the other mineral fibres. Often there are more than two layers of the defined shell-core fibres and so the batt may comprise alternating layers of the defined shell-core fibres with layers of the other fibres.

It is explained in WO 2004/110945 that an advantage of the defined shell-core fibres is that they have improved

resistance to shrinkage or sintering, especially under conditions where there is restricted access of air (as applies in normal fire protection and heat insulation products that are sandwiched between structural sheets or are otherwise in a confined space). The various heterogeneous products described above all have the advantage that the defined shell-core fibres will resist sintering or shrinkage even when the other mineral fibres do undergo sintering or shrinkage. Accordingly the heterogeneous distribution of the defined shell-core fibres is able to provide a matrix of the defined shell-core fibres within the overall product so as to maintain heat insulation and fire protection properties even after sintering or shrinkage of the other mineral fibres has initiated.

Particular problems arise where conventional batts are joined to one another, either as panels or as batts fitted into closed spaces, because shrinkage of the batts tends to occur at elevated temperatures and the batts are made wholly of conventional fibres. This shrinkage can result in gaps forming between adjacent batts, and this is clearly undesirable. Appropriate arrangement of the layers of defined shell-core fibres can minimise or eliminate that problem.

For instance, if the heterogeneous distribution involves at least one layer of the shell-core fibres extending over the entire area of the batt, usually over the entire area of either or both of the outer faces of the batt, this or each layer will tend to maintain the area dimensions of the batt even when the conventional fibres are tending to undergo shrinkage.

Instead of or in addition to this, if there is at least one layer of the defined shell-core fibres extending in the thickness dimension of the batt, this will tend to maintain the thickness dimension. It is particularly valuable to provide a layer of the defined shell-core fibres extending throughout the thickness direction around

some or all of the four edges of the batt, i.e, around the rim of the batt. This again tends to prevent the risk of shrinkage and the formation of gaps between batts.

For instance, a preferred product has its periphery
5 defined wholly or mainly by a layer of the defined shell core fibres which extends through the thickness of the batt and the remainder of the batt may have a heterogeneous tufted or layered distribution of both types of fibre, as discussed above.

10 Conventional bonded batts of conventional fibres include bonding agent which is preferably a heat-curable organic bonding agent and this contributes to the ignition loss of the product. Typically the amount of organic bonding agent in conventional heat insulating and fire
15 protection mineral fibre batts has to be kept at well below 1 or 1.2% (calculated as ignition loss) in order to minimise the exotherm (and the potential risk of shrinkage and sintering) that will occur when the batt is exposed to sufficiently high temperatures. Often endothermic material
20 is included in the batt to absorb some of the exotherm.

A technical problem that arises from the need to minimise the amount of organic binder is that the batt is not as strong as would be desirable from the point of view of handling it during manufacture, transport and
25 installation, and permanently installing it in its desired position. This problem is minimised when the batt is encased between structural sheets as, for instance, fire boards, but is a major problem when the batt is not provided with structural sheets on each face and is being
30 installed in confined spaces such as in floors, ceilings or walls or in chimneys or around ovens.

According to a third aspect of the invention we provide heat insulating fire protection products which comprise a bonded batt of mineral fibres comprising the
35 defined shell-core fibres and wherein the batt contains combustible binder providing the batt with an ignition loss

of above 1.2%, generally above for instance up to 2% or 2.5, or even 3%.

These products have a reduced risk of collapsing and can be made without the necessity to include any endothermic material and, as a result of the increased amount of organic binder, are much easier to handle, transport and install. Extra strength means that they can be fixed in position more easily, with reduced risk of falling away from the surfaces to which they are fixed.

The batts containing these increased amounts of binder can be formed solely of the defined shell-core fibres, or of mixtures with other mineral fibres, for instance heterogeneous layered or tufted mixtures as described above, or homogeneous mixtures.

A further aspect of the invention includes the use of all products described and defined in WO 2004/110945 and/or made by the method of the first aspect of the invention and/or the products defined in the second and third aspects of the invention in applications where the unique properties of the defined shell-core fibres makes their use of particular merit.

These uses include applications where a low oxygen environment is likely to arise due to limited supply of oxygen, such as in chimneys, linings in furnaces, fire safe box, safe-deposit box, floating floors, panels, suspended ceilings with steel cassettes as well as sandwich panels, fire doors and in maritime fire insulation. The maritime uses may be vertical (ie bulkhead) or horizontal (ie deck).

Other uses include applications where the reduced risk of shrinking is particularly valuable, when the product must, in order to be used, be tested in a fire testing furnace. In a fire testing furnace the oxygen level is around 4 to 6% (normal 21%). Combustion of binder and oil in a product will lower the oxygen level furthermore. Thus the invention provides uses in applications where the product must be tested in accordance with ISO 834 and/or according to the hydrocarbon time-temperature curve. Such

applications include maritime fire insulation tested according to ISO834 (the normal time-temperature curve in a fire test) and tested according to the hydrocarbon time-temperature curve and fire protection of steel construction.

General insulation applications, such as pipe insulation, are also valuable.

CLAIMS:

1. A method of making a mineral fibre batt comprising
5 shell-core fibres and other fibres, the method comprising
fiberising a melt to form a cloud of said other fibres,
collecting said other fibres as a web by air-laying and
forming the web into a batt,
wherein the shell-core fibres are formed of a
10 silicate network and comprise silicon, calcium, magnesium,
iron, aluminium, oxygen and optionally alkali metal atoms
and have an analysis expressed as percent by weight oxides
including at least 3% FeO and 0 to 8% alkali metal oxide
and at least 5% MgO, and in the shell-core fibres at least
15 70% of the iron is ferric and the fibres have a core
surrounded by an outer surface layer less than 1 micron
thick in which the peak concentration of magnesium atoms
is at least 1.5 times the concentration of magnesium atoms
in the total fibre,
20 characterised in that the method comprises including
the shell-core fibres in the batt by mixing the shell-core
fibres with the other fibres after formation of the other
fibres but before completion of formation of the batt from
the web.
25
2. A method according to claim 1 in which the other
fibres are formed of a silicate network and comprise
silicon, calcium, magnesium, iron, aluminium, oxygen and
optionally alkali metal atoms and have an analysis
30 expressed as percent by weight oxides including at least
3% FeO and 0 to 8% alkali metal oxide and at least 5% MgO.
3. A method according to claim 2 in which the overall
35 composition of the shell-core fibres is essentially the
same as the overall composition of the other fibres.

4. A method according to any preceding claim in which the mixing of the shell-core fibres with the other fibres is carried out so as to produce a substantially homogeneous distribution of shell-core fibres throughout
5 the batt.

5. A method according to any of claims 1 to 3 in which the mixing of the shell-core fibres with the other fibres is carried out so as to produce a heterogeneous
10 distribution of the shell-core fibres in the batt.

6. A method according to any preceding claim in which the shell-core fibres are mixed with the other fibres by injecting the shell-core fibres into the cloud of other
15 fibres before collection as a web.

7. A method according to claim 6 in which the shell-core fibres are introduced as individual fibres.

20 8. A method according to claim 6 in which the shell-core fibres are introduced as tufts.

9. A method according to any of claims 1 to 5 in which the mixing of the shell-core fibres with the other fibres
25 takes place after the collection of the other fibres as a web.

10. A method according to any preceding claim in which the shell-core fibres are waste fibres from a process of
30 producing fibres of essentially the same composition as the said other fibres and the waste fibres have been subject before the mixing step to a heat treatment comprising exposing the fibres under oxidising conditions to a controlled increased temperature which is above the
35 temperature at which oxidation of the iron in the fibres occurs but which is below the temperature at which substantial network crystallisation occurs and thereby

oxidising the ferrous iron to provide fibres in which at least 70% of the total iron is ferric.

11. A method according to claim 10 in which the waste
5 fibres are recycled fibres taken from the same production line as that producing the batt and/or from a different production line producing other batts in the same facility.
12. A method according to claim 10 or claim 11 in which
10 the waste fibres are subjected to granulation before heat treatment.
13. Heat insulation or fire protection product comprising
15 shell-core fibres as defined in claim 1 heterogeneously distributed with other mineral fibres within a batt having a density of 10 to 300kg/m³, optionally sandwiched between foils and/or structural sheets.
14. A product according to claim 13 comprising tufts of
20 the shell-core fibres in admixture with tufts or fibres of the other mineral fibres.
15. A product according to claim 13 comprising at least
25 one layer of the shell-core fibres and at least one layer of the other mineral fibres.
16. A product according to claim 13 in the form of a
30 panel comprising a layer of the shell-core fibres extending substantially entirely over at least one of the outer faces of the batt.
17. A product according to claim 13 comprising at least
35 one layer of the shell-core fibres extending in the thickness dimension of the batt.

18. A product according to claim 17 in which there is a layer of the shell-core fibres extending throughout the thickness direction of the batt around some or all of the edges of the batt.

5

19. A heat insulation or fire protection product comprising a bonded batt comprising shell-core fibres as defined in claim 1 and binder in an amount providing an ignition loss of at least 1.2%.

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20. Use of a product of the method of any of claims 1 to 12 or the product of any of claims 13 to 19 as heat insulation or fire protection material in an application where a low oxygen environment is likely to arise.

15

21. Use according to claim 20 wherein the product is used in a chimney, as a lining in a furnace, in a fire safe box, in a safe-deposit box, in an floating floor, in a panel, in a suspended ceiling with steel cassettes, in a sandwich panel, in a fire door or as maritime fire insulation.

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22. Use of a product of the method of any of claims 1 to 12 or a product of any of claims 13 to 19 in an application which must be tested in a fire testing furnace.

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INTERNATIONAL SEARCH REPORT

 International application No
 PCT/EP2005/013567

A. CLASSIFICATION OF SUBJECT MATTER C03C13/06 C03C13/00 C03C1/00 D04H1/42 C03B37/05 E04B1/80				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) C03C C03B D04H E04B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
P, X	WO 2004/110945 A (ROCKWOOL INTERNATIONAL A/S; JENSEN, SOREN, LUND) 23 December 2004 (2004-12-23) cited in the application page 16, line 17 - line 24; claims -----	1-22		
A	WO 99/51535 A (ROCKWOOL INTERNATIONAL A/S; LARSEN, PETER; GROVE-RASMUSSEN, SVEND) 14 October 1999 (1999-10-14) page 5, line 3 - page 6, line 29 -----	1-22		
A	US 6 319 866 B1 (JENSEN SOREN LUND ET AL) 20 November 2001 (2001-11-20) column 3, line 12 - line 20 abstract ----- -/--	1-22		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table border="0"> <tr> <td style="vertical-align: top;"> *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed </td> <td style="vertical-align: top;"> *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family </td> </tr> </table>			*A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family
A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family			
Date of the actual completion of the international search 8 March 2006		Date of mailing of the international search report 15/03/2006		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Reedijk, A		

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/013567

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2005/013567

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			AU 3597199 A	25-10-1999
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